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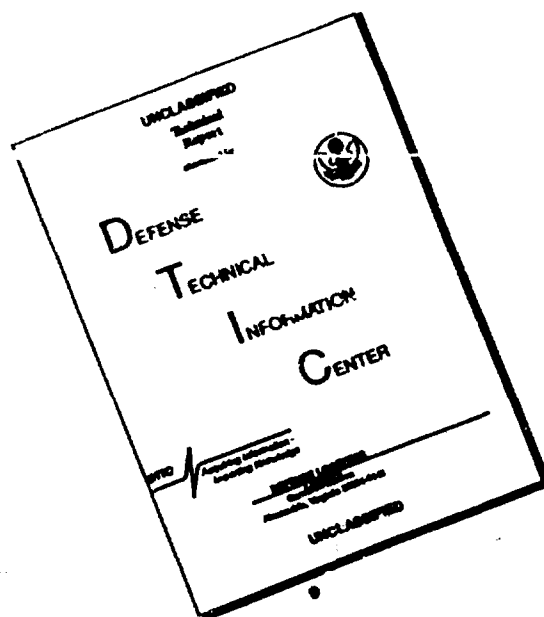
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## CATALYTIC OXIDATION OF TRIPHENYL PHOSPHITE WITH FERRIC ION-MODIFIED CHROMATOGRAPHIC SILICA

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### ABSTRACT

Triphenyl phosphite oxidation to triphenyl phosphate has been found to be catalyzed by ferric ion-modified silica stationary phases in liquid chromatographic columns. The oxidation chemistry found in this study indicates that special precautions are needed for aromatic phosphite analyses where columns may contain metals leached from stainless steel equipment. The catalytic activity can be suppressed by inert gas purging of the mobile phase to reduce its oxygen content and treating the column with a reductant to deactivate stationary phase oxidative sites. The activity can be restored by treating the deactivated column with appropriate oxidants. The on-column triphenyl phosphite oxidation reaction also can be used as a diagnostic tool to provide evidence on column contaminations with immobilized active metals and their location within the column. Using the ideal liquid chromatographic reactor model with an inert standard method, kinetic parameters for the on-column triphenyl phosphite oxidation reaction can be evaluated.

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### INTRODUCTION

On a number of occasions, metal ions have been doped onto stationary phases to alter retention or selectivity for high performance liquid chromatographic separations[1-4]. Some complications from reactions of solutes during liquid chromatographic separation on metal-modified stationary phase surfaces also have been recognized. Such complications may be a result of complexation or tenacious adsorption[5-8], or a consequence of catalytic activities of stationary phase surfaces [9-12]. To-date, the catalytic activities of liquid chromatographic columns have been recognized in only a few instances. One noteworthy example is the catalyzed oxidation of hydroquinone-type compounds during analysis on normal phase metal-contaminated silica columns[9], on metal-contaminated reverse-phase columns[10], and in styrene-divinylbenzene resin-based ion-exclusion chromatography [11]. Applications of catalytically active columns in liquid chromatographic reactors are even fewer. Here, we report on the catalytic activity of ferric ion-modified silica stationary phases for organic aromatic phosphite oxidations, their possible use as a diagnostic tool, and how this catalytic activity might be useful in chromatographic reactor operations.

Organic phosphite oxidations to phosphate have been of interest for years. Among reagents that may be used to accomplish this are ozone, dinitrogen tetroxide, alkyl hypochlorites (e.g., EtOCl), amine oxides ( $R_3NO$ ), quinones, sulfur dioxide, sulfur chloride ( $SO_2Cl_2$ ), hydrogen peroxide, and peracids[13,14], as well as nitric acid[15]. Catalytic processes by which organic phosphites are oxidized directly with oxygen also have been described, mostly in the patent literature. Catalysts include copper and copper

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oxide[16], aluminum oxide and vanadium pentoxide[17], transition metal carboxylates[18], a halogen component with a cationic cocatalyst[19], and more recently,  $P_2O_5$ [20]. However, all of these oxidation processes involved batch reactor operations with reaction times of the order of an hour to several days for complete conversion.

For this initial exploratory work, we employed ferric ion-modified chromatographic silicas with special retention properties in a column that functions as a liquid chromatographic reactor to study the triphenyl phosphite oxidation to triphenyl phosphate. This material prepared in aqueous media as described elsewhere, had higher activity for catalyzing the hydroquinone oxidation to benzoquinone[21] than did earlier materials. The triphenyl phosphite oxidation study reported herein is intended to provide more information on ferric ion-modified silica. While column catalytic oxidative activity may cause complications in aromatic phosphite analyses, such activity can be adapted as a diagnostic tool for detecting column metal ion contamination, as with other metal ion catalyzed reactions in chromatography[9]. Furthermore, ferric ion catalytic activity for doped columns can be put on a quantitative basis and utilized in chromatographic reactors for kinetic studies of dissolved solutes and possibly for converting them on a quantitative basis.

### MATERIALS

The ferric ion-modified silica prepared in aqueous media used here has been described elsewhere[21]. Other preparative procedures have also been described [22,23]. Triphenyl phosphite, triphenyl

phosphate and phenol were obtained from Aldrich and used without further purification. All solvents were HPLC grade obtained from Burdick & Jackson.

#### EXPERIMENTAL METHODS

The high-performance liquid chromatographic system used here incorporated a Beckman 110B solvent delivery pump, a Beckman Series 210 four-port sample valve with a 20  $\mu$ L sample loop, a Perkin-Elmer LC-55 variable wavelength spectrophotometer detector adjusted to a detection wavelength of 260 nm, an HP 3396A integrator and, in parallel, a Sargent-Welch model SRG recorder. A Perkin-Elmer LC-235 diode array detector was used as appropriate to scan and compare the UV spectra of standard triphenyl phosphite, phenol, triphenyl phosphate and the product wave from the triphenyl phosphite oxidation.

Columns (10 cm x 4.6 mm ID) were slurry-packed with 10  $\mu$ m Spherisorb S10W silicas and ferric ion-modified S10W Spherisorb silicas prepared in aqueous media. Isopropyl alcohol was used at about 6000 psi with an in-house slurry-packing apparatus[24]. For column contamination and diagnostic studies, a frequently used and previously studied[9] 30 cm x 4.6 mm ID Workhorse Spherisorb S10W silica column (Pegis Chemical Co.) was employed.

For the degassing treatment of the mobile phase used in Table 1, helium purging at a flow rate of 1.0 cm<sup>3</sup>/min through the mobile phase in a Kontes HPLC Reservoir System (500 mL) was used.

The triphenyl phosphite oxidation reaction was conducted at temperatures between 25 and 45°C and flow rates between 0.5 to 4.0 mL/min with a mobile phase of 10% methyl t-butyl ether (MTBE) in

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hexane. Temperature control was obtained as described previously using a column jacket[22,23], but with a Brinkmann, RM 20 LAUDA water circulating bath as a reservoir. The in-house packed bare silica column, as well as the new ferric ion-modified silica column were used under similar conditions for comparison of triphenyl phosphite oxidative activity.

A triphenyl phosphite solution (1.25 mM) in the mobile phase was used for the oxidation studies. Because of the short triphenyl phosphite retention time, fast reaction rate, and relatively long triphenyl phosphate residence time, an "external standard method" was adapted to the evaluation of kinetic data from chromatographic reactor experiments. This was possible because of the reproducible sample volumes that can be introduced to the column through liquid chromatographic procedures. The external inert standard mixture was a 0.5 mM toluene-0.725 mM triphenyl phosphate mixture in the mobile phase. Whereas toluene was the inert used for obtaining the column dead volume  $V_d$ , triphenyl phosphate was the external inert standard used for correlating the data. Basically, this method works as follows: the reactant mixture is introduced into the column at particular operating conditions; a toluene/triphenyl phosphate mixture is then injected under exactly the same operating conditions immediately after the complete elution of the reactant pulse. The reactant peak area ( $A_r$ ) in the first elution chromatogram was measured using a planimetric method[25,26], and the eluted inert chromatographic peak area from the second injection ( $A_i$ ) was also measured by planimetry. Five repeated injections were performed at each flow rate, and reproducible peak areas were observed.

The mobile phase for diagnostic studies was 15% dioxane in hexane. This mobile phase was also used in experiments with in-

house packed ferric ion-modified silica and unmodified silica columns. The capacity factors of triphenyl phosphite, triphenyl phosphate and phenol were measured with both mobile phases used in this study, and were calculated based on  $k' = (V_R - V_0)/V_0$ . Here  $V_R$  is the retention volume of the solute, and  $V_0$  is the column dead volume based on toluene. Five repeated injections were performed and reproducible capacity factors within one percent or better resulted.

### RESULTS AND DISCUSSION

Figure 1 shows a comparison of chromatograms for triphenyl phosphite samples on unmodified silica and ferric ion-modified silica columns. On introduction of a 1.25 mM triphenyl phosphite solution sample onto the unmodified silica column at a flow rate of 1.0 mL/min, only the reactant peak, and a small phenol peak (impurity in the reactant) with a retention time of 4.85 minutes can be observed on the chromatogram (Figure 1a). There is no indication of triphenyl phosphate formation. On the ferric ion-modified silica column under corresponding conditions, introduction of a triphenyl phosphite sample resulted in evidence for triphenyl phosphate formation. Figure 1b clearly shows that in addition to the reactant peak and a small bump on the product wave with a retention time of 7.35 minutes, there is a continuous band starting with reactant peak elution that ends at about 10 minutes after sample injection. This is a consequence of the relatively long phosphate retention compared to phosphite. The catalytic oxidation is initiated at the column inlet and stops at the outlet. The result is a continuous, broad product wave, part of which is

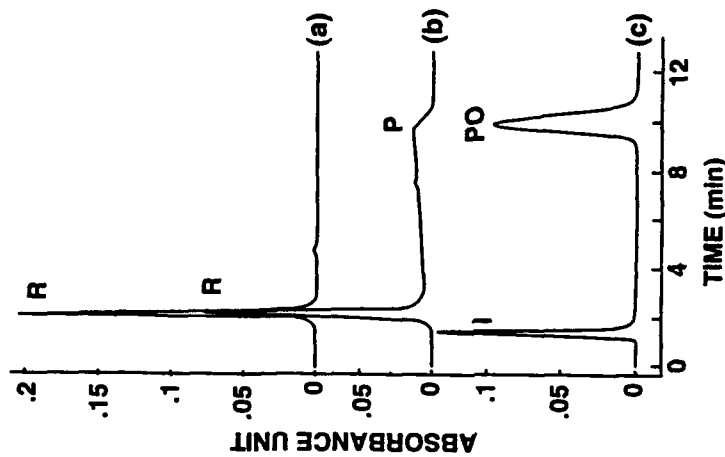


FIGURE 1.

Chromatograms of 1.25 mM triphenyl phosphite at 25.0°C in (a) a bare silica column at flow rate of 1.0 mL/min, and (b) an iron(III)-silica column at flow rate of 1.0 mL/min; where (c) is the chromatogram of a standard mixture of 0.5 mM toluene and 0.725 mM triphenyl phosphite in an iron(III) silica column at flow rate of 1.0 mL/min. Mobile phase: 10% methyl t-butyl ether in hexane; sample size: 20  $\mu$ L.

I: Inert standard, toluene.

PO: Standard triphenyl phosphate.

R: Triphenyl phosphite reactant.

P: Triphenyl phosphate formed due to triphenyl phosphite oxidation in the column.

Small bumps in (a) and (b) are phenol impurity.

superimposed in the Gaussian reactant peak. The product wave identity was confirmed using a retention time method involving the injection of a known sample of triphenyl phosphite under the same condition as indicated by Figure 1c. The center of the back end of the wave corresponds to the retention of triphenyl phosphate formed at the column inlet. A diode array detector also was used to scan and compare the ultraviolet spectra of different sections of the wave with the standard triphenyl phosphite UV spectrum (obtained by the injection of triphenyl phosphite standard under the same conditions). The reinjection of the effluent into the pure silica column further confirmed that the oxidation product was essentially triphenyl phosphite, and that the amount of eluted phenol impurity was constant. The change in phenol retention time on the ferric ion-modified silica column is due to the strong phenol hydroxylic group interactions with immobilized ferric ions on silica, as described elsewhere[21].

Flow rate variation experiments provide further evidence that the triphenyl phosphite oxidation to phosphate is catalyzed by the ferric ion-modified silica stationary phase. Figure 2 shows the results obtained for a ferric ion-modified silica column at several flow rates at a temperature of 35.0°C. As the flow rate decreases (or the residence time of triphenyl phosphite increases), it can be seen that the reactant peak area decreases and the product wave increases. At a flow rate of 0.5 mL/min, almost complete phosphite oxidation occurred, as indicated in Figure 2c; the small bump overlapping part of the product wave is the phenol impurity in the reactant. As noted before[9,27], such flow rate variation experiments strongly support the hypothesis that the triphenyl phosphite oxidation occurs on the column stationary phase surface and establishes the identification of the catalytic activity of the ferric ion-modified silica for triphenyl phosphite oxidation.

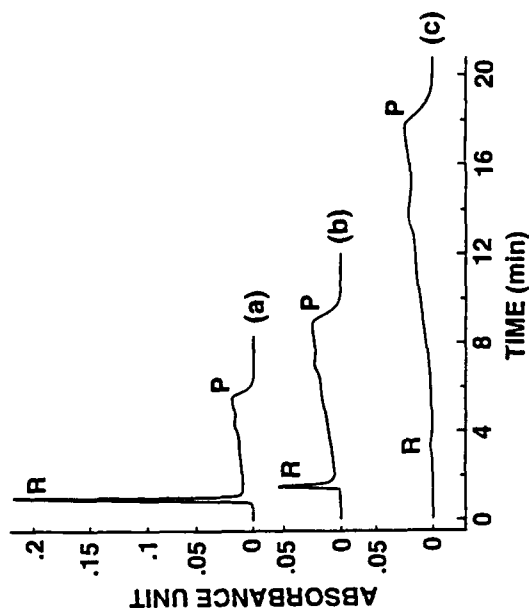


FIGURE 2. Series of liquid reactor chromatograms for triphenyl phosphite oxidation catalyzed by iron(III)-silica at 35.0°C. (a) at flow rate of 1.5 mL/min, (b) at flow rate of 1.0 mL/min, and (c) at flow rate of 0.5 mL/min. For other conditions, see Figure 1 caption.

#### Stationary and Mobile Phases Treatments

As demonstrated above, the ferric ion-modified silica column is unusually active for conversion of low triphenyl phosphite concentrations to triphenyl phosphate, since the required reaction time is of the order of minutes even under mild conditions. Chromatographic reactor experiments also allow further characterization of the nature of the triphenyl phosphite oxidation reaction. Table 1 shows the results for a series of treatments of the mobile phase and the ferric ion-modified stationary phase. The column reactivity from these sequences of treatments is referenced to the initial experimental procedure(A). After purging the mobile phase with helium to remove dissolved oxygen (B), no reduction in the oxidation activity was observed for the first injection;

TABLE 1  
Effects of Mobile Phase and Column Treatments<sup>a</sup>

Stage of treatment	A <sub>p</sub> /A <sub>i</sub> <sup>b</sup>	Relative activity in the column
A. Mobile phase sonicated for 1 hr for 18 hours	1.24±0.03	1.0
B. Mobile phase purged with helium		
	1.23 <sup>c</sup>	0.99
	1.13 <sup>c</sup>	0.91
	1.03 <sup>c</sup>	0.83
C. Column treated with reducing reagent <sup>d</sup> , (PhO) <sub>3</sub> P	0.78±0.05	0.63
D. Further column treatment with reducing reagent <sup>d</sup> , (PhO) <sub>3</sub> P	0.68±0.05	0.55
E. Column treated with reducing reagent <sup>e</sup> , (hydroquinone)	0.21±0.03	0.17
F. Column treated with oxidizing reagent <sup>f</sup> , (benzoquinone)	0.71±0.05	0.57
G. New mobile phase sonicated for 1 hour and after flow for 1 hr	1.23±0.05	0.99

<sup>a</sup>Chromatographic conditions:

Column DD(2)-43, ferric ion-modified silica; mobile phase: 10 % methyl t-butyl ether in hexane; flow rate: 0.924 mL/min; sample: 20 µL of 1.24 mM triphenyl phosphite; detection wavelength: 260 nm.

<sup>b</sup>Area ratio of the product wave to the standard triphenyl phosphite peak area.

<sup>c</sup>First injection of 20 µL of 1.24 mM triphenyl phosphite, followed by second and third injections, which result in different activities due to the absence of oxygen in the mobile phase.

<sup>d</sup>Ten repetitive injections of 100 µL of 5 mM (PhO)<sub>3</sub>P.

<sup>e</sup>Ten repetitive injections of 100 µL of 5 mM (PhO)<sub>3</sub>P.

<sup>f</sup>Ten repetitive injections of 100 µL of 5 mM benzoquinone.

however, with the second and third injections of the reactant, sequential reductions of column activity resulted. This result supports a redox mechanism for the triphenyl phosphite oxidation. Since helium purging of the mobile phase should not affect the ferric ion surface state, the initial oxidation activity might be expected for the first phosphite pulse. However, with additional pulses of phosphite, the number of active Fe(III) sites would be

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reduced because of the absence of mobile phase oxygen needed for reoxidizing the immobilized ferrous ions to the ferric state.

Subsequent reductive treatment of the column with triphenyl phosphite (C) and (D) resulted in about a 50% decrease of the column reactivity. While activity was reduced still further with hydroquinone (E), some oxidative activity was retained even after a series of treatments.

Column reactivity could be partly regenerated by introduction of benzoquinone (F), and completely regenerated with normal mobile phase flow (G). The benzoquinone treatment restored the catalytic activity to a level comparable to what it was after the triphenyl phosphite column reduction. The final treatment with the normal mobile phase containing dissolved oxygen from air restored the original column activity, providing evidence for the role of oxygen as a strong oxidant for restoring ferrous ions to the ferric ion state.

### Triphenyl Phosphite Oxidation as a Diagnostic Tool

One attractive application of the iron-catalyzed, on-column triphenyl phosphite oxidation would be as a potential diagnostic tool for detection of column contamination with iron or other transition metals from stainless steel. This would be similar to the application of the hydroquinone oxidation[9]. It is particularly pertinent, since so many modern arrays of HPLC equipment contain significant quantities of stainless steel, which are subjected to corrosion and leaching during continuous usage with many different types of solvent mixtures[28-31]. Leached metals, especially iron(the main component) but possibly others, such as chromium, could be deposited by ion exchange or precipitation and accumulated in the column over long periods of



use. Catalytic activity could, in turn, cause problems with quantitative analysis. With the challenge to chromatographers to detect and understand such problems without unpacking the column, the search for simple probe reactions to identify their origins becomes meaningful.

In Figure 3, the result is shown of using the on-column triphenyl phosphite oxidation as a diagnostic probe, to detect the existence of metal ions in a frequently used Regis Workhorse silica column that was known to be contaminated. The two chromatograms in the figure show a large product wave, presumably triphenyl phosphate, in addition to the triphenyl phosphite peak. At two flow rates, 1.0 and 2.0 mL/min, the wave areas correspond well with the on-column catalytic oxidation hypothesis, and indicate that the stationary phase surface is responsible for catalytic activities. Thus, using the on-column triphenyl phosphite to-triphenyl phosphate reaction allows the detection of the metal ions on the silica surfaces of the Regis Workhorse column. This was also possible with the hydroquinone oxidation to benzoquinone[9], which was described earlier. However, the product waves are more pronounced for the triphenyl phosphite oxidation here than for the previous hydroquinone oxidation[9]. Furthermore, the shape of this wave and the time of its maximum suggests that the largest amount of transition metal is deposited at the column inlet but some minor amounts are deposited throughout the column. This is consistent with previous conclusions about this column[9].

Because the Regis Workhorse silica column is longer than the in-house, packed ferric ion-modified silica column, and also appears to have only leached material deposited on the stationary phase surfaces, a different mobile phase, 15% dioxane in hexane, was used for the diagnostic studies. With this mobile phase, the

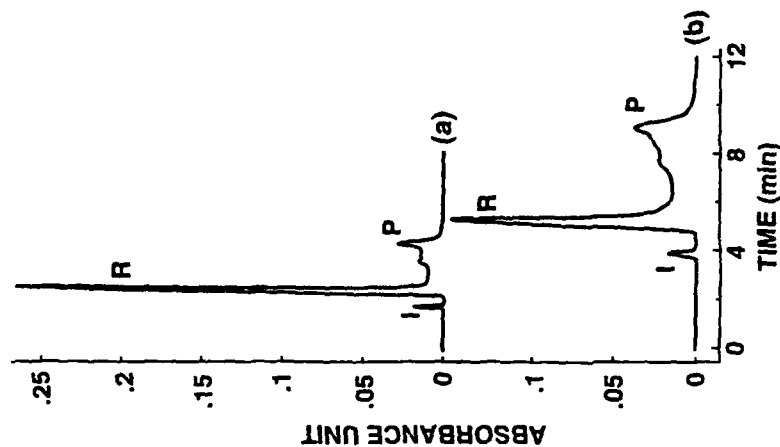


FIGURE 3. Triphenyl phosphite on-column oxidation as a diagnostic tool at 25.0°C. Column: Regis Workhorse silica that has been contaminated by frequent use. Mobile phase: 15% dioxane in hexane. (a) flow rate 2.0 mL/min; (b) flow rate 1.0 mL/min. For other conditions, see Figure 1 caption.

retention time of triphenyl phosphate tends to be shortened while the residence time of triphenyl phosphite reactant tends to be lengthened (longer reacting time), as can be seen from Table 2, where various columns are compared using capacity factors pertinent to this work. An unmodified silica column was also used to compare the triphenyl phosphite oxidation in the mobile phase and the

TABLE 2

Capacity Factors  $k''$  With The Columns of This Study

Column and Mobile Phase	Triphenyl phosphite	Phenol	Triphenyl phosphate
A. DD(2)-43 <sup>(1)</sup> , Fe <sup>3+</sup> /SiO <sub>2</sub> column			
10% MTBE/Hexane	0.22	3.37	4.84
15% Dioxane/Hexane	0.37	0.98	1.45
B. DD(2)-29 <sup>(2)</sup> , unmodified silica column			
10% MTBE/Hexane	0.11	2.41	3.24
15% Dioxane/Hexane	0.23	0.82	1.08
C. Contaminated Regis Workhorse silica column <sup>(3)</sup>			
10% MTBE/Hexane	0.20	2.89	4.80
15% Dioxane/Hexane	0.31	0.94	1.31
			1.27 <sup>**</sup>

\* Capacity factors are based on  $k' = (V_R - V_0)/V_0$ . Where  $V_0$  is the retention volume of the solute, and  $V_R$  is the retention volume of toluene here.

\*\* This is based on maximum for P in Figure 3.

(1) DD(2)-43 is the 10 cm x 4.6 mm ID ferric ion-modified silica column used in this study. Toluene retention volume is 1.422 cm<sup>3</sup> for this column.

(2) DD(2)-29 is the 10 cm x 4.6 mm ID unmodified silica column used in this study. Toluene retention volume is 1.419 cm<sup>3</sup> for the column.

(3) This column gives a toluene retention volume of 3.945 cm<sup>3</sup>.

possibility of unmodified silica surface catalysis. But the clean silica column showed no indication of triphenyl phosphate formation with the same mobile phases. Because of the changes in capacity factors for the Regis Workhorse silica compared to unmodified silica, we can speculate that silica surface modification and possible contamination has occurred. The nature of the Regis Workhorse silica column activity for the triphenyl phosphite oxidation tends to confirm the column contamination hypothesis and even suggests its location. Thus, the triphenyl phosphite oxidation provides an additional diagnostic tool for the detection of column contamination with iron or other transition metals.

## Reaction Kinetics

Using the ideal chromatographic reactor model, we investigated the possibility that reaction kinetic parameters might be evaluated, treating the oxidation as a pseudo-first order reaction, as described earlier. The microscopic mass balance for a first-order or pseudo-first-order reactions coupled with proper initial and boundary conditions[32,33], results in the following equation with the inert standard method:

$$\ln(A_0/A_1) = \ln(A_0/A_1) \text{ at } t=0 - k_s * t_s \quad (1)$$

where  $A_0$  is the peak area of the reactant on the reactor chromatogram,  $A_1$  is the peak area of inert standard under the same conditions, and  $k_s$  is the apparent first-order or pseudo-first-order rate constant. In the more general situation  $k_s$  contains contributions from reaction in both the mobile phase and stationary phase so that

$$k_s = k_m * (t_s/t_r) + k_s * (t_s/t_r) \quad (2)$$

where  $k_m$  and  $k_s$  are the rate constants in the mobile phase and in the stationary phase, respectively;  $t_s$  and  $t_r$  are the reactant residence times in the mobile phase and stationary phase, and  $t_s$  is the total residence time of reactant in the column( $t_s+t_r$ ). If  $k_m$  is small compared to  $k_s$ , then by setting  $k_s$  to zero, equation (3) can be simplified to give

$$k_s = k_s * (t_s/t_r) \quad (3)$$

Substituting Eq.(3) into Eq(1), gives

$$\ln (A_0/A_1) = \ln (A_0/A_1)_{t=0} - k_p \cdot t_0 \quad (4)$$

Flow rate variation experiments at controlled temperatures (similar to those shown in Figure 2) can provide the  $A_0/A_1$  data for various stationary phase residence times  $t_0$  [25,32,33]. By plotting  $\ln(A_0/A_1)$  vs.  $t_0$  and taking the slope of the line, a value for the pseudo-first order rate constant,  $k_p$ , can be obtained.

Oxygen solubility in the organic mobile phase used here is ca. 10 mM[23], well in excess of the maximum triphenyl phosphite concentration in the pulses of our experiments (1.25mM). With the ferric ion-modified silica stable under our experimental conditions [21], the number of catalytically active sites for the reaction is essentially constant. With these assumptions the triphenyl phosphite oxidation can be treated as a pseudo-first-order reaction, with catalyst and oxygen concentration incorporated in the stationary phase rate constant, so that  $k_p$  can be calculated through equation(4).

Figure 4 shows the plots of  $\ln(A_0/A_1)$  versus  $t_0$  at three temperatures. The reasonably good linearity of the plots seems to support the pseudo-first order reaction treatment for the triphenyl phosphite reaction. From the plots,  $k_p$  values are calculated with results tabulated in Table 3. Batch study of this reaction at 25.0°C for 1.25 mM (PhO)<sub>3</sub>P in 10% MTBE:hexane solution (150 mL) without catalyst(under air) gave a (pseudo)first-order apparent rate constant of  $7.1 \times 10^{-6} \text{ s}^{-1}$ , validating the neglect of the uncatalyzed reaction in the mobile phase.

Applying the Arrhenius equation, a value of  $12.0 \pm 1.5 \text{ kcal/mole}$  for the apparent activation energy of the reaction was obtained.

Figure 5 is a demonstration of temperature effects on the triphenyl phosphite oxidation. As the column temperature increases

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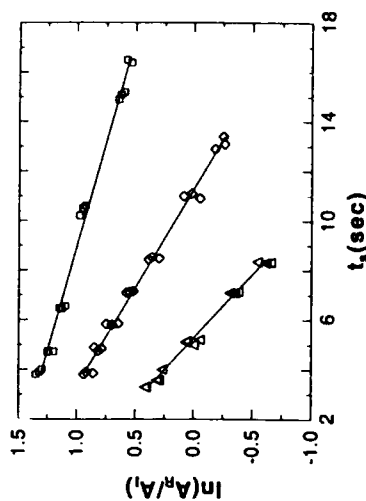


FIGURE 4. Pseudo-first order kinetic plots for triphenyl phosphite oxidation in iron(III)-silica column at (□) 25.0°C, (○) 35.0°C, and (Δ) 45.0°C. (see text)

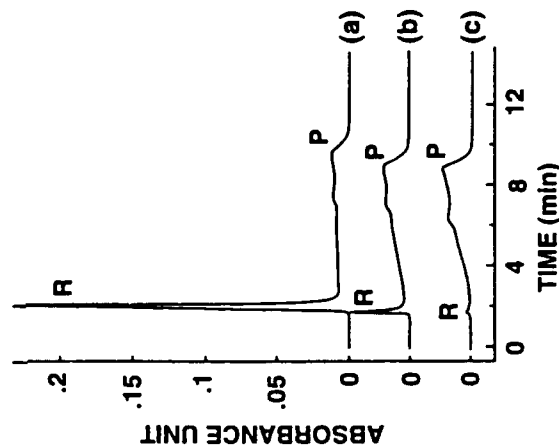


FIGURE 5. Series of liquid reactor chromatograms for triphenyl phosphite oxidation catalyzed by iron(III)-silica at a flow rate of 1.0 mL/min at (a) 25.0°C, (b) 35.0°C and (c) 45.0°C. For other conditions, see Figure 1 caption.

TABLE 3

Pseudo-First-Order Reaction Rate Constants for Triphenyl Phosphite Oxidation to Triphenyl Phosphate

Temp. (°C)	$k_a$ (sec <sup>-1</sup> )
25.0	0.053±0.004
35.0	0.116±0.003
45.0	0.186±0.014

Activation Energy  $E_a = 12.0 \pm 1.5$  kcal/mole.

from 25.0°C to 45.0°C at a constant flow rate, the residence time in the stationary phase does not change greatly. However, the reaction rate increases significantly. At 45°C, even though the triphenyl phosphite residence time ( $t_r$ ) on the stationary phase was only about 20 seconds, almost complete conversion to triphenyl phosphate resulted. The reinjection of the effluent in a clean silica column (described in Experimental Methods) indicated again that the oxidation product was only triphenyl phosphate. The results shown in Figure 5, also suggest that where reactions in a column may cause an analytical problem, it is a good practice to lower operating temperatures to minimize undesired conversions.

### CONCLUSIONS

Ferric ion-modified silica can catalyze triphenyl phosphite oxidation to triphenyl phosphate. Because of this oxidation activity, precautions are appropriate when performing HPLC triaryl phosphite analyses. The on-column triphenyl phosphite oxidation also can provide a diagnostic probe for the detection of column contamination with iron. Ferric ion-modified silicas prepared in

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aqueous media can be used in liquid chromatographic reactors to provide a new and effective means for conversion of low triphenyl phosphite concentrations under mild conditions. Furthermore, application of the ideal liquid chromatographic reactor approach allows the evaluation of kinetic information on the reaction. The oxidation reaction is apparently first order with respect to triphenyl phosphite and dependent on both immobilized ferric ion and oxygen concentrations.

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